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אני, (שם המבקש, מענו ולגבי גוף מאוגד - מקום התאגדות)

I, (Name and address of applicant, and in case of body corporate-place of incorporation)

Inventors:

מציאים:

1. אשוחוש ג'ושי
ASHUTOSH Joshi

2. קולודני יורי
KOLODNY Yuri

3. קריסל איתי
KREISEL Itay

4. ששון יואל
SASSON Yoel

YISSUM RESEARCH DEVELOPMENT COMPANY

OF THE HEBREW UNIVERSITY OF JERUSALEM

P.O.Box 39135

91390 Jerusalem

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Beit Zera

D.N. Emek Hayarden 15135

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ייצור מוגבר של רדיקלים הידרוקסיליים

(בעברית)

(Hebrew)

ENHANCED GENERATION OF HYDROXYL RADICALS

(באנגלית)

(English)

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ENHANCED GENERATION OF HYDROXYL RADICALS

ENHANCED GENERATION OF HYDROXYL RADICALS

Field of the Invention

The present invention relates to a method for enhancing the formation of
5 hydroxyl radicals in water environment in the presence of hydrogen
peroxide, by the combined effect of UV irradiation, dissolved oxygen, and
magnesium oxide as a catalyst.

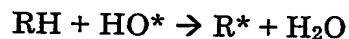
Background of the Invention

10 Hydroxyl radical (HO^*) is one of the strongest oxidants that is available in
the natural world and in the chemist's tool box. This species is extremely
reactive and degrades promptly any available organic molecule. Hydroxyl
radicals, likewise other reactive oxygen species, are also a very potent
biocide which vigorously attacks microorganisms and tissues, damaging
15 cell membranes lipids, proteins, carbohydrates and DNA. The hydroxyl
radical reactions are extremely fast, having rate constants of from 10^7 to
 $10^9 \text{ M}^{-1} \text{ sec}^{-1}$. Consequently the hydroxyl radical only diffuses the
equivalent of 5-10 of its molecular diameter before it reacts [E. Cadenas:
Ann. Rev. Biochem.58 (1989) 79]. Interestingly, hydroxyl radicals and
20 other reactive oxygen species were recently realized as a cellular signaling
device [E.g., Van Breusegem et al.: Plant Sci. 161 (2001)405-414], as well

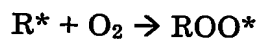
as a biological weapon used by the immune system for killing bacteria
[Wentworth P. et al.: Science 298 (2002) 2195-9].

Hydroxide radicals injure cell membrane lipids via the following chain
5 mechanism:

a) Detachment of a hydrogen radical randomly from a fatty acid, leading
to the formation of an alkyl radical:



b) The alkyl radical reacts instantly with oxygen (which is available in
10 aerobic environment) to yield an alkylhydroperoxide derivative:

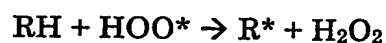


c) The alkyl hydroperoxide reacts with water to generate an alcohol and a
hydroperoxyl radical:

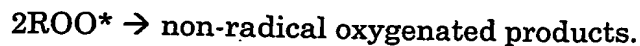


15 The transformation of a fatty acid skeleton into an alcohol renders the
destruction of the membrane structure and consequently the collapse of
the cell wall and the death of the organism.

d) The hydroperoxyl radical absorbs a hydrogen radical from another fatty
acid molecule to yield an alkyl radical that subsequently reacts with
20 oxygen, as shown in step b):



The hydrogen peroxide formed becomes the source of additional hydroxyl radicals which renew the cycle. This chain process propagates until a termination step such as the following one takes place:



5 A fundamental feature of hydroxyl radicals (and other reactive oxygen species) is the benign nature of their decomposition products. No chemicals are formed as a result of their application in various water treatments but water. Interestingly, recent studies suggest that reactive oxygen species are also a signaling device and even a defense tool for
10 numerous plants and living organisms [E.g., Van Breusegem et al.: Plant Sci. 161 (2001)405-414].

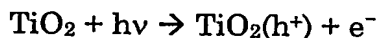
Several methods for the generation of hydroxyl radicals are known, based mainly on hydrogen peroxide as the source. The simplest and the most
15 accepted methodology is based on the Fenton reaction where ferrous ion reacts with hydrogen peroxide in an acidic media as follows [Legrini O.: Chem. Rev. 93 (1993) 671-98]:



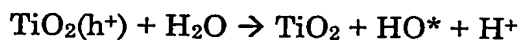
This reaction is made catalytic predominantly under the effect of UV
20 irradiation of the wavelength greater than 300 nm, which allows the recycling of Fe^{+3} to the original Fe^{+2} , which process is named "Photo-Fenton" reaction. The main drawback of the Fenton type procedures is

their strong dependence on pH. Thus the above reaction occurs only under acidic conditions, preferably at pH= 2.5-3.0.[Andreozzi R. et al.: Catalysis Today 53 (1999) 51-9]. Consequently the Fenton scheme is not practicable under the numerous situations where acidic media cannot be used, such as in ballast water treatment, for example.

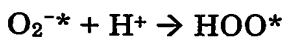
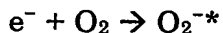
Another procedure for the formation of hydroxyl, and hydroperoxyl, radicals uses photocatalysis together with semi-conductors such as TiO_2 . Upon irradiation of TiO_2 particle by the light having wavelength about 315-395 nm, an electron is ejected, generating a "hole" on the particle surface:



The "hole" interacts with water to produce a hydroxyl radical:



The free electron reacts with oxygen molecule to produce an anion of superoxide radical which is protonated to yield a hydroperoxyl radical:



Another widespread technique for the making of hydroxyl radical is direct photolysis of hydrogen peroxide under UV irradiation:



This procedure suffers from low efficacy due to the very low molar extinction coefficient of the hydrogen peroxide molecule (about $19 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 254 nm at neutral pH [Baxendale J.H.: Trans. Faraday Soc. 53 (1957)344].

5

Using EPR techniques, Giamello E. et al. showed [J. Phys. Chem. 97(1993) 5735-40] that reactive oxygen species were formed upon contact of hydrogen peroxide with the surface of magnesium oxide in an aqueous environment. These authors also observed a highly unexpected stability of hydroxyl radicals adsorbed on the MgO surface, wherein the radicals were stable at temperatures as high as 200°C .

10

It is an object of this invention to provide a high efficacy method for producing hydroxyl radicals in aqueous environment using UV irradiation of hydrogen peroxide solutions.

15

It is another object of this invention to provide a method for producing hydroxyl radicals in water solutions of hydrogen peroxide and oxygen, combining UV irradiation with a catalytic effect of magnesium oxide.

20

Other objects and advantages of present invention will appear as description proceeds.

Summary of the Invention

This invention provides a method for enhancing the generation of hydroxyl radicals in aqueous mixtures containing hydrogen peroxide comprising: i) supplying oxygen or air to said mixture; ii) supplying magnesium oxide to said mixture; iii) irradiating said mixture with UV light, preferably having a wavelength of from 190 to 390 nm; and iv) mixing said mixture. Said aqueous mixture is an aqueous solution or suspension. The initial concentration of hydrogen peroxide is from 2 ppm to 250 ppm, preferably 10 ppm to 50 ppm. Magnesium oxide is preferably added to the mixture in one portion of from 2 ppm to 250 ppm, and more preferably from 10 ppm to 50 ppm. Oxygen is supplied as air or pure oxygen, preferably to saturation.

Brief Description of the Drawings

The above and other characteristics and advantages of the invention will be more readily apparent through the following examples, and with reference to the appended drawings, wherein:

Fig. 1. Shows the effect of individual factors on the formation of hydroxyl radicals;

Fig. 2. is a HPLC chromatogram of salicylic and hydroxysalicylic acid; and

Fig. 3. is a table summarizing conversion rates of salicylic acid under various conditions.

Detailed Description of the Invention

It has now been surprisingly found that the presence of magnesium oxide
5 in an aqueous mixture containing hydrogen peroxide and oxygen leads to enhanced formation of hydroxyl radicals under UV irradiation. Without wishing to be limited by any particular theory, the inventors believe that magnesium oxide is a strong catalyst for the conversion of hydrogen peroxide into hydroxyl radicals in water environment provided the system
10 is irradiated by a UV light. This phenomenon provides particularly good results in the presence of oxygen. The synergic combination of hydrogen peroxide, oxygen, magnesium oxide and UV irradiation provides an effective new means for the generation of hydroxyl radicals in water. Surprisingly, even in the absence of hydrogen peroxide, a significant
15 amount of hydroxyl radicals are formed in water in the presence of oxygen and magnesium oxide. In a preferred embodiment of the present invention, hydrogen peroxide is added to an aqueous solution in which the formation of hydroxyl radicals is desired, and magnesium oxide is injected as a suspension while mixing the aqueous solution, introducing into it
20 oxygen, and irradiating it by UV. Any commercially available UV irradiation source can be used.

In a preferred embodiment of the method according to this invention, the initial concentration of hydrogen peroxide is from 2 ppm to 250 ppm, the solution is saturated with oxygen, and magnesium oxide in suspension is injected as a catalyst to a concentration from 2 ppm to 250 ppm. Oxygen is
5 preferably introduced into the mixture by injection of oxygen or air.

In one of the preferred embodiments of the invention, the peroxide radicals serve for the treatment of ballast water. In a preferred embodiment of this invention, hydrogen peroxide is added to sea water,
10 intended to serve as ballast water, to a concentration of from 10 to 50 ppm, air or oxygen is finely dispersed to saturate the mixture, and magnesium oxide is added to a concentration of from 10 ppm to 50 ppm.

This invention thus provides a method for enhancing the generation of
15 hydroxyl radicals in aqueous mixtures containing hydrogen peroxide comprising i) supplying oxygen to said mixture; ii) supplying magnesium oxide to said mixture; iii) irradiating said mixture with UV light; and iv) mixing said mixture for a period sufficient to generate the desired amount of radicals, wherein said desired amount of radicals may be an amount
20 sufficient to reach a required effect in the mixture, for example a biocidal effect. Said desired amount of radicals may be a required predetermined quantity. Hydroxyl radicals may be quantified by physical or chemical

methods known in the art, such as measuring redox potentials, or reacting hydroxyl radicals with a trapping agent such as salicylic acid, etc. Said aqueous mixture can be a solution or suspension. Air or oxygen is supplied in any suitable manner that can inject and homogenize it into the aqueous solution, preferably providing saturation. According to a preferred embodiment of the invention the UV radiation has a wavelength of from 190 to 390 nm. Magnesium oxide is preferably added to the mixture in one portion. The period that enables the generation of required amount of radicals depends on the type of application of said mixture, and may be typically from few seconds to several hours, for example from 3 seconds to 5 hours, and preferably it is from 30 seconds to 100 minutes. The mixture may be irradiated essentially during the whole period that is set for the generation of hydroxyl radicals, and also oxygen may be supplied to the mixture during the whole of said period, or, alternatively, the application of UV and supplying oxygen may last only a few seconds, if the required effect is attained that quickly in said type of application.

In a preferred embodiment of this invention, the pH of the aqueous solution, in which the formation of hydroxyl radicals is desired, has a value of from 5 to 10, and preferably from 7.2 to 9.7.

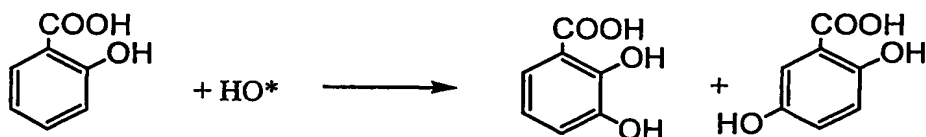
The described process can be used whenever the increased concentration of hydroxyl radicals is desirable, an example being processing ballast water, industrial waste waters, municipal waste waters, etc. The method of this invention may be thus used, for example, for the purification of sea water or municipal effluent water, however without being limited to these examples.

The invention will be further described and illustrated by the following examples.

10 Examples

Quantifying hydroxyl radicals

The formation of hydroxyl radicals was quantified by reacting the radicals with salicylic acid [H. Kaur et al.: Methods in Enzymology 233 (1994) 67-82] to form 2,3-dihydroxybenzoic acid 2,5-dihydroxybenzoic acid, and by detecting these products by HPLC with a UV detector (See Fig. 2), using column RP-18, 80% phosphate buffer pH 6.5 + 20% methanol, flow rate 1 ml/min, and λ_{\max} 300 nm.



The degree and rate of the conversion to dihydroxybenzoic acid is proportional to the amount of hydroxyl radicals generated in a given system.

Example 1

5 Reaction was carried out in a one liter beaker equipped with a stirrer, into which a medium pressure mercury UV lamp in a quartz sleeve, Immersion Lamp TQ 150W, was immersed. Approximately half the lamp was immersed. Tap water passed continuously through quartz jacket to cool it. The total volume of reaction mixture was 800 ml. Illuminated length was
10 41 mm. Salicylic acid (Fluka, purity > 99.5 %), 500 ppm in 400 ml seawater, and 400 ml seawater were stirred with a magnetic stirrer, and the pH of the solution was adjusted to 7.85 with 0.5 % NaOH. The irradiation continued for 90 min. Samples were withdrawn at 10, 20, 40, 60 and 90 min, and analyzed by HPLC. The conversion rates were
15 calculated as ratios of hydroxysalicylic/(salicylic + hydroxysalicylic) (see Figs. 1 and 3).

Example 2

The reaction was started as in Example 1, but 20 ppm (16 mg) of magnesium oxide (obtained from Aldrich, purity 98%) was added to 800 ml
20 of the reaction mixture after the pH adjustment, and after 5 min the irradiation started, and continued for 90 min.

Example 3

The reaction was started as in Example 1, but hydrogen peroxide, 20 ppm in 400 ml seawater, was added to salicylic acid, 500 ppm in 400 ml seawater, pH was adjusted to 7.85 with 0.5 % NaOH, and the mixture was
5 then irradiated during 90 min.

Example 4

The reaction was started as in Example 3, but 20 ppm (16 mg) of magnesium oxide was added to 800 ml of the reaction mixture after the pH adjustment, and only then the irradiation started.

10

Example 5

The reaction was started as in Example 1, but after the pH adjustment, purging of the mixture started, oxygen being fed at a rate of 50 ml/min through a glass tube of diameter 0.5 cm. After 10 min, the irradiation
15 started, and continued for 90 min.

Example 6

The reaction was started as in Example 2, but after the addition of magnesium oxide, and 5 min stirring, purging of the mixture with oxygen
20 started, oxygen being introduced through a glass tube of diameter 0.5 cm. After 10 min, the irradiation started, and continued for 90 min.

Example 7

The reaction was started as in Example 3, but after the pH adjustment, the mixture was purged with oxygen which was introduced through a glass tube of diameter 0.5 cm. After 10 min, the irradiation started, and
5 continued for 90 min.

Example 8

The reaction was started as in Example 4, but after adding magnesium oxide and 5 min stirring, purging of the mixture with oxygen started, oxygen being introduced through a glass tube of diameter 0.5 cm. After 10
10 min, the irradiation started, and continued for 90 min. The pH at 90 min was 7.91. The initial and final temperature of the reaction mixture were 23°C and 25.5°C, respectively, and the initial and final redox potential of the reaction mixture were 180 mV and 110 mV, respectively. The superior generation of hydroxyl radicals in the system $\text{MgO}/\text{H}_2\text{O}_2/\text{O}_2$ can be seen in
15 Figs. 1 and 3.

Example 9

Some of the enhanced activity, seen in the mixtures containing MgO, might be attributed to the increased basicity in the presence of solid MgO. Therefore, two reactions were performed comparing the effect of MgO with
20 ~~the effect~~ of sodium hydroxide. Two mixtures contained 250 ppm salicylic acid, 30 ppm hydrogen peroxide, and they were irradiated by UV. The first mixture further contained 250 ppm MgO, its pH was adjusted to 7.8 at the

beginning of the reaction, and rose to 9.38 after 90 minutes. The second mixture did not contain MgO and its initial pH was adjusted to 9.55 by NaOH. Magnesium oxide had stronger effect even when compared to the effect of sodium hydroxide, pH 9.55, which further demonstrates the
5 phenomenon of catalytic properties of MgO.

While the invention has been described using some specific examples, many modifications and variations are possible. It is therefore understood that the invention is not intended to be limited in any way, other than by
10 the scope of the appended claims.

CLAIMS

1. A method for enhancing the generation of hydroxyl radicals (OH^*) in aqueous mixtures containing hydrogen peroxide comprising
 - i) supplying oxygen to said mixture;
 - ii) supplying magnesium oxide to said mixture as a catalyst;
 - iii) irradiating said mixture with UV light; and
 - iv) mixing said mixture.
2. The method of claim 1, wherein the aqueous mixture is an aqueous solution or suspension.
3. The method of claim 1, wherein hydrogen peroxide has an initial concentration of from 2 to 250 ppm.
4. The method of claim 1, wherein oxygen is supplied by injecting of air or oxygen into the mixture.
5. The method of claim 1, wherein oxygen is supplied to saturation.
6. The method of claim 1, wherein said UV radiation has wavelength of from 190 to 390 nm.

7. The method of claim 1, wherein magnesium oxide is added to the mixture to a concentration of from 2 ppm to 250 ppm.
8. The method of any one of claims 1 to 7, wherein the initial concentration of hydrogen peroxide is from 10 to 50 ppm, and the initial concentration of magnesium oxide is from 10 to 50 ppm.
9. The method of any one of claims 1 to 8, wherein the pH of said mixture has a value of from 5 to 10.
10. The method of claim 9, wherein said pH has a value of 7.2 to 9.7.
11. The method of claim 1, wherein said mixing is carried out for a period of time sufficient to generate the desired amount or radicals.
12. The method of claim 11, wherein said desired amount of radicals is an amount sufficient to reach a required biocidal effect in the mixture.
13. The method of claim 11, wherein said period lasts from 3 seconds to 5 hours.

14. The method of claim 13, wherein said period lasts from 30 second to 100 minutes.
15. The method of claim 11, wherein said period lasts more than 5 hours.
16. The method of claim 11, wherein said desired amount of radicals is a predetermined quantity.
17. The method of claim 11, wherein generated radicals are quantified by a physical or chemical method.
18. The method of claim 17, wherein said chemical method comprises reacting hydroxyl radicals with salicylic acid.

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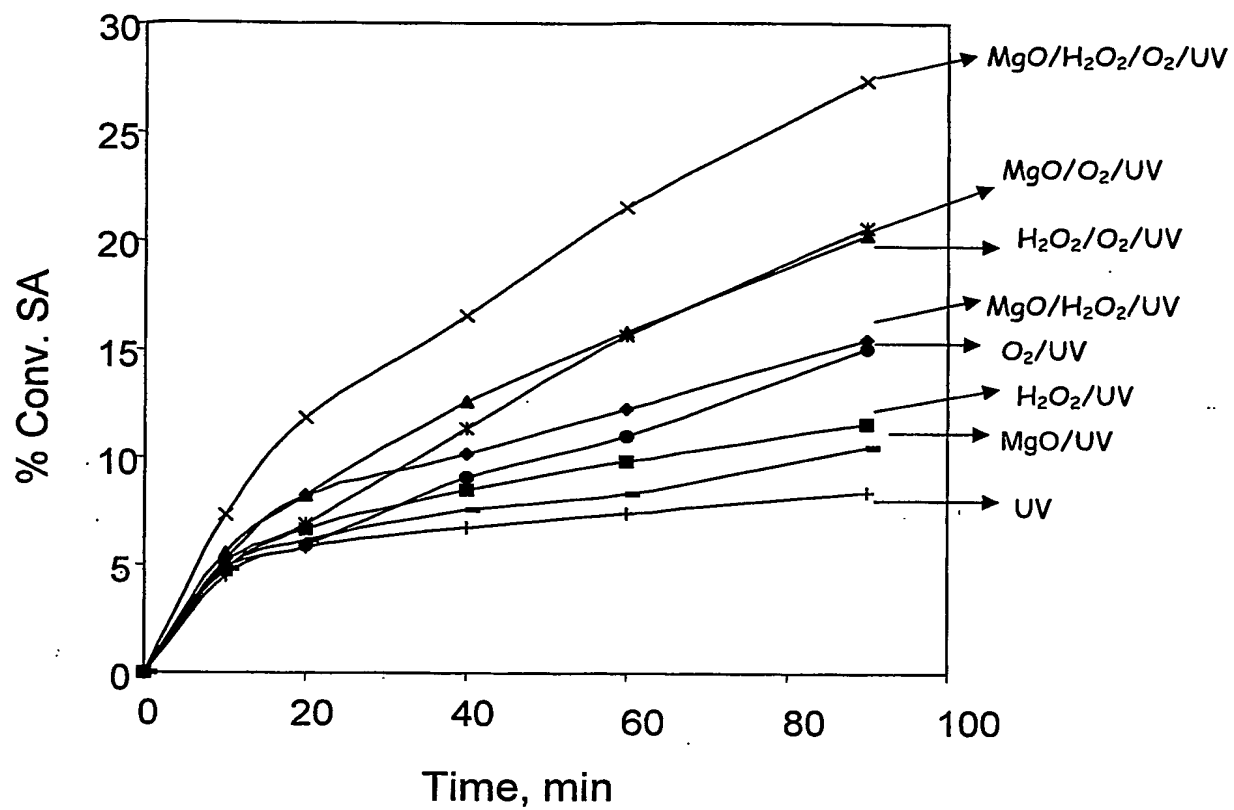


Fig. 1

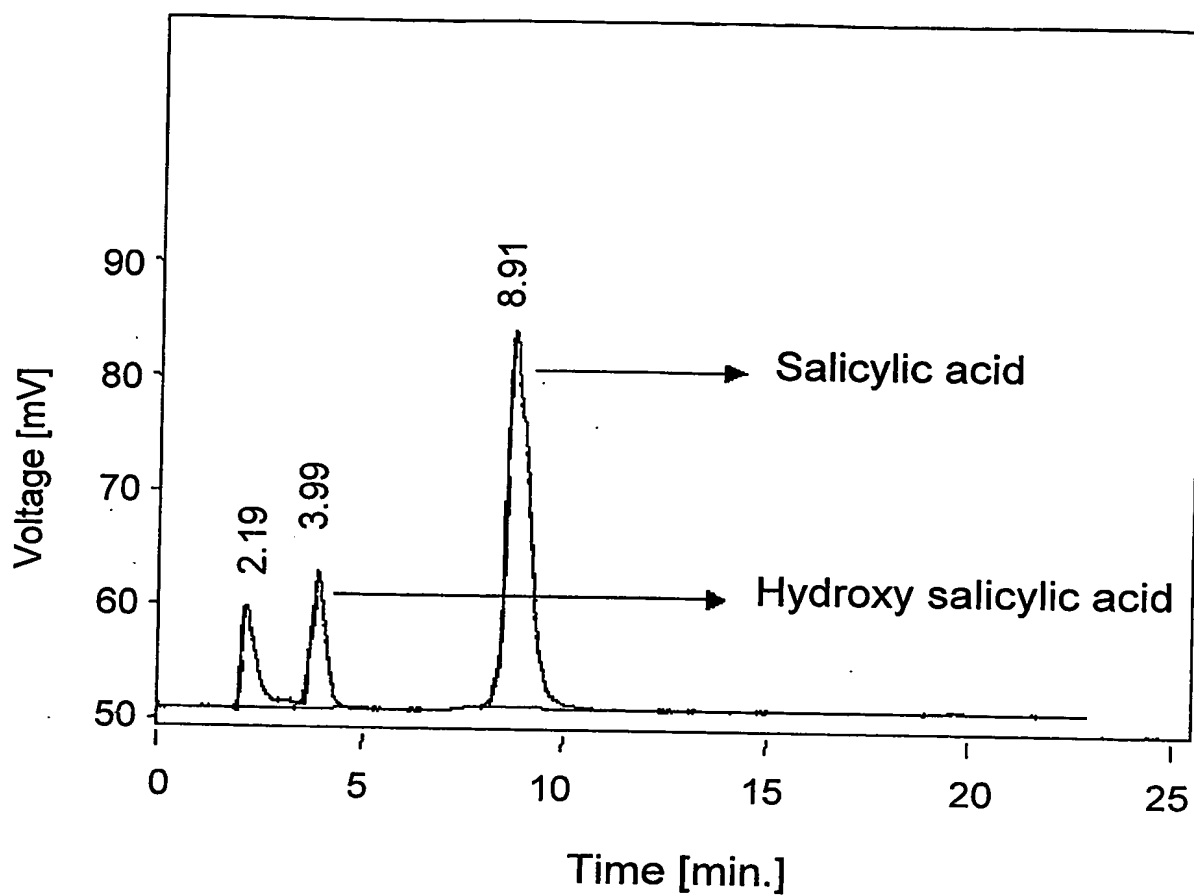


Fig. 2

Run No	Reaction conditions	H ₂ O ₂ (ppm)	MgO (ppm)	Conv. of SA in 90 min (%)	Conv. of SA in 20 min (%)
1	SA/UV	0	0	8.42	5.8
2	SA/UV/MgO	0	20	10.51	6.12
3	SA/UV/H ₂ O ₂	10	0	11.56	6.64
4	SA/UV/H ₂ O ₂ /MgO	10	20	15.42	8.2
5	SA/UV/ O ₂	0	0	15.08	5.9
6	SA/UV/MgO/ O ₂	0	20	20.56	6.89
7	SA/UV/H ₂ O ₂ /O ₂	10	0	20.31	8.26
8	SA/UV/H ₂ O ₂ /MgO/O ₂	10	20	27.37	11.76

Fig. 3

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